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(54) ELECTROMAGNETIC WAVE ABSORBING MATERIAL AND MANUFACTURE THEREOF

(57) Abstract:

PROBLEM TO BE SOLVED: To provide an electromagnetic wave absorbing material, together with its manufacturing method, which comprises an electromagnetic wave

absorbing performance with less weight and high manufacturing efficiency.

SOLUTION: Water is added to the powder material wherein 20-60 wt.% of ferrite, 5-30 wt.%, with bulk density being 0.15 or less, of calcium silicate hydrate (ultra-light calcium silicate hydrate), cement, siliceous material, and fabric reinforcing material are mixed to provide a kneaded material, which is extrusion-molded or dehydration-molded before hydrothermal process. Thus, an electromagnetic wave absorbing material is provided. Here, since an ultra- light calcium silicate hydrate is used, the increase in weight of electromagnetic wave absorbing material which comprises ferrite is suppressed for lighter electromagnetic wave absorbing material.

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AB   The invention relates to an electromagnetic wave absorber contg. **cement**, **silica**, super-light-wt. **calcium silicate hydrate** having a bulk sp. gr. of .ltoreq. 0.15 5-30, fiber reinforcing material, and ferrite 20-60 %.
ST   electromagnetic wave absorber **calcium silicate hydrate**
IT   Electromagnetic wave
        (absorber; electromagnetic wave absorber contg. **cement** and **silica** and **calcium silicate hydrate** and fiber and ferrite)
IT   Cellulose pulp
       Cement (construction material)
     Electromagnetic shields
        (electromagnetic wave absorber contg. **cement** and **silica** and **calcium silicate hydrate** and fiber and ferrite)
IT   Ferrites

Translation of the relevant parts of Reference 2, Japanese Patent Laid-Open No. 2001-28492

CLAIMS

[Claim 1]

An electromagnetic wave absorber characterized in comprising cement, a silica raw material, an ultralight calcium silicate hydrate, a fiber reinforcing material, and a ferrite,

said ferrite being contained in an amount of 20 to 60 wt%;

said ultralight calcium silicate hydrate having a bulk specific gravity of 0.15 or less and being contained in an amount of 5 to 30 wt%.

[Claim 2]

An electromagnetic wave absorber according to claim 1, which is characterized in that said calcium silicate hydrate is crystalline Xonotlite, crystalline tobermorite.

[Claim 3]

A method of producing an electromagnetic wave absorber, characterized by extrusion molding of a mixed and kneaded material prepared by adding water to a row powder material, which is prepared by mixing ferrite in an amount of 20 to 60 wt%, calcium silicate hydrate of a bulk specific gravity of 0.15 or less in an amount of 20 to 60wt%, content, a silica raw material and a fiber reinforcing material.

[Claim 4]

A method of producing an electromagnetic wave absorber, characterized by dehydration molding of a mixed and kneaded material prepared by adding water to a row powder material, which is prepared by mixing ferrite in an amount of 20 to 60 wt%, calcium silicate hydrate of a bulk specific gravity of 0.15 or less in an amount of 20 to 60wt%, content, a silica raw material and a

fiber reinforcing material.

[Claim 5]

A method of producing an electromagnetic wave absorber according to claim 3 or 4, characterized in that as the calcium silicate hydrate, quasicrystal CSH is used.

[Sections 0007 to 0047]

[0007]

[Means for Solving the Problem]

An electromagnetic wave absorber relating to the 1st invention of this invention is characterized in comprising cement, a silica raw material, an ultralight calcium silicate hydrate, a fiber reinforcing material, and a ferrite,

said ferrite being contained in an amount of 20 to 60 wt%;

said ultralight calcium silicate hydrate having a bulk specific gravity of 0.15 or less and being contained in an amount of 5 to 30 wt%.

[0008]

Here, as said fiber reinforcing material, a fiber reinforcing material of organic fibers or inorganic fibers for reinforcement can be used. The organic fibers include a cellulose fiber, a polypropylene fiber, an aramid fiber, etc. The inorganic fibers include glass fibers, carbon fibers, silicon carbide fibers, stainless steel fibers, aluminum textiles, etc.

[0009]

The ultralight calcium silicate hydrate is calcium silicate hydrate having a bulk specific gravity of 0.15 or less. Those of 0.06-0.08g/cm^3 based on JIS K6220 is preferable. As such a calcium silicate hydrate, those prepared by a hydrothermal synthesis processing in an autoclave of a starring type. The concrete examples include calcium silicate hydrates tobermorite (5CaO, $6SiO_2$, and $5H_2O$), xonotlite (6CaO, $6SiO_2$, and H_2O) and CSH (it is an amorphous calcium silicate hydrate and they are an intermediate and the quasicrystal generated when a calcium silicate hydrate carries out a hydration reaction.), etc. Regarding the bulk specific gravity of the ultralight calcium silicate hydrate,

xonotlite has 0.06 g/cm^3 (based on JIS K6220), for example, and CSH has 0.08 g/cm^3 (based on JIS K6220). Xonotlite is obtained by drying a calcium silicate slurry at 120 degrees with a spray dryer.

[0010]

The ferrite is preferably contained in an amount of 20 to 60 wt%, specially 30 to 50wt%. In the case where it is not more than 20 wt%, sufficient electromagnetic-wave-absorbing performance is not obtained, while in the case where it is more than 60 wt%, weight increasing of the electromagnetic wave absorber is caused.

[0011]

The calcium silicate hydrate is preferably contained in an amount of 5 to 30 wt%, especially 10 to 20 wt%. In the case where it is not more than 5 wt%, an effect to save the weight of the electromagnetic wave absorber is not provided, while in the case where it is more than 30wt%, since, when a plate material of calcium silicate is produced for example by an extrusion molding, the extrusion molding property become wrong, it is necessary to add an extrusion auxiliary agent in a increased amount.

[0012]

According to the 1st invention, by using calcium silicate hydrate of a bulk specific gravity of 0.15 or less, the electromagnetic wave absorber can be lightened by preventing high-weighting of the electromagnetic wave absorber including ferrite adsorbing electromagnetic wave.

[0013]

Since ferrite is contained in the electromagnetic wave absorber, electromagnetic waves which entered into an inside of an electromagnetic wave absorber are transformed into thermal energy with amplitude permeability which a ferrite has, and an electromagnetic wave incident is absorbed in an electromagnetic wave absorber. Therefore, the property for the electromagnetic-wave-absorbing is securable for a plate made from a calcium silicate.

[0014]

Thus, ferrite is contained in an necessary amount in order to keep the

property for the electromagnetic-wave-absorbing. However, since ferrite has a specific high gravity, a high weight increase of the electromagnetic wave absorber occurs. The calcium silicate hydrate having a specific gravity of 0.15 or less is contained, the high weight increase by ferrite content can be suppressed and a weight saving of an electromagnetic wave absorber can be attained.

[0015]

Since it is different from an electromagnetic-wave-absorbing wall, in which each separate plate is combined into a composite, a slurry is prepared from the above materials and the electromagnetic wave absorber is made from the slurry. Thus, the electromagnetic wave absorber can be easily molded and the productivity can be thus increased.

[0016]

The electromagnetic wave absorber relating to the 2nd invention of this invention is characterized in that the calcium silicate hydrate is crystalline xonotlite or crystalline tobermorite in the 1st invention. That is, since it is supposed that xonotlite has heat resistance against 1000 degrees and it is supposed that tobermorite has heat resistance against 650 degrees, it is dramatically stable thermally and sufficient fire resistance efficiency can be given to an electromagnetic wave absorber.

[0017]

A method of producing an electromagnetic wave absorber concerning the 3rd invention of this invention is characterized by extrusion molding of a mixed and kneaded material prepared by adding water to a row powder material, which is prepared by mixing ferrite in an amount of 20 to 60 wt%, calcium silicate hydrate of a bulk specific gravity of 0.15 or less in an amount of 20 to 60wt%, content, a silica raw material and a fiber reinforcing material.

[0018]

Specifically optimum dose of water can be added to the powder raw material to make a kneaded material with mobility, such as gel. The kneaded material is then extruded to obtain a calcium silicate mold. Then calcium silicate mold is treated by hydrothermal synthesis processing to produce the

electromagnetic wave absorber. Thus, since the conventional hydrothermal synthesis processing can be used, the production of the electromagnetic wave absorber can be easily and the productivity can be increased.

[0019]

Te concrete contents of said fiber reinforcing material and said ultralight calcium silicate hydrate are the same as indicated in the 1st invention.

[0020]

According to the method of producing an electromagnetic wave absorber relating to the 3rd invention, a plate with the flat surface, a plate in which a surface pattern is comparatively shallow, a three-dimensional structure, etc. can be effectively manufactured by carrying out extrusion molding of the kneaded material. Since extrusion molding is a forming process with little unevenness by specific gravity difference of each raw material, various materials for construction rich in design feeling can be formed, which include a ceiling cornice, a sacrifice edge, and a window frame, as well as the flat plate. In particular, when a concave-convex pattern rich in design feeling is applied by a production by ladling, repealing power occurs in the concave-convex pattern thus obtained. Therefore, it is difficult to make a clear pattern. According to the method of producing the electromagnetic wave absorber of the present invention, since the extruded mold is soft like a clay, a clear concave-convex pattern can be made. After the slurry is extruded into a pate form, it can be cured by in a high pressure and high temperature autoclave as usually.

[0021]

The method of producing an electromagnetic wave absorber relating to the 4th invention is characterized by dehydration molding of a mixed and kneaded material prepared by adding water to a row powder material, which is prepared by mixing ferrite in an amount of 20 to 60 wt%, calcium silicate hydrate of a bulk specific gravity of 0.15 or less in an amount of 20 to 60wt%, content, a silica raw material and a fiber reinforcing material.

[0022]

The concrete contents of said ultralight calcium silicate hydrate and said fiber reinforcing material are the same as indicated to the 1st invention. The

dehydration molding can be effectively used, when a plate having a surface pattern with comparatively deep grooves is formed. After a suitable amount of water is added to the powder material and pressed for dehydrating to mold a plate, it can be cured by in a high pressure and high temperature autoclave as usually.

[0023]

The method of an electromagnetic wave absorber concerning the 5th invention of this invention, quasicrystal CSH is used as a calcium silicate hydrate in the 3rd invention or the 4th invention. Since CSH can be synthesized at a low temperature in an autoclave of a stirring type, the manufacturing cost of the electromagnetic wave absorber can be reduced. Since CSH is an intermediate of a hydration reaction of a calcium silicate hydrate, CSH expresses a property as a binder and enhances the strength of the electromagnetic wave absorber by crystallizing CSH finally at curing of the mold of calcium silicate in water and heat.

[0024]

[Embodiment of the Invention]

(The 1st embodiment)

Cement, a silica raw material, a fiber reinforcing material, ferrite in amount of 20 to 60wt% and calcium silicate hydrate having a bulk specific gravity of 0.15 or less in an amount of 5 to 30 wt% are mixed to a powder material. A suitable amount of water is added to the powder material and mixed, stirred and kneaded with an extrusion additional agent of a cellulose derivative. After the kneaded material is obtained, the mixture material is put into an extruder to make a plate. The plate thus molded is cured in an autoclave in a high temperature and at a high pressure for reactive curing. Thus, the electromagnetic wave absorber of this embodiment is manufactured.

[0025]

(The 2nd embodiment)

First ferrite in an amount of 20 to 60 wt%, calcium silicate hydrate having a bulk specific gravity of 0.15 or less in an amount of 5 to 30 wt%, cement, silica raw material and a fiber reinforcing material are mixed to a powder material. A

slurry is formed by mixing and stirring a binder with the powder material in a mixer to laminate the powder material by the binder. Thereafter, the slurry is dried to fix the binder on the powder material. This mixing and stirring reduce resolving with water while the lamination effect is kept. This treatment is a necessary timing to prevent the adhesion of each particle of the powder material.

[0026]

When a binder is an SBR latex system, 3 to 4 wt% is preferred to said powder raw material as an outside rate weight ratio. The effect by adding the binder of less than 3 wt% is low, and the effect by adding the binder of more than 4 wt% is slight and incombustibility is low.

[0027]

Next, the total amount of water and the remaining raw materials of a quantity suitable in this mixer are supplied, and predetermined time mixing and stirring are carried out to arrange so as to obtain a suitable slurry concentration. After the slurry is pored in a mold, a dehydrating press is carried out and a plate is fabricated. At the end, reactive curing in an autoclave at a high temperature and in a high pressure is performed to manufacture a plate. Thus, the electromagnetic wave absorber of this embodiment is manufactured.

[0028]

[Example]

Next, the examples and the comparative examples concerning this invention are explained, referring to Table 1. Here, Table 1 shows the blending ratio of the raw material in the examples and the comparative examples. This invention is not limited to the following examples. In the following explanation, pulp, a polypropylene fiber, and the chemical admixture of organic textiles are mineral impalpable powder. As ferrite particles, Zn-ferrite sintered particles of a diameter of 0.1-6.0 mm were used. A quicklime was mixed with water to obtain a milk and the milk was treated though 60-mesh to obtain a lime milk for use.

[0029]

[Table 1]

	Examples					Comparative examples			Remark
	1	2	3	4	5	1	2	3	Wt%
Cement	22	22	22	22	22	22	30	30	
Fly ash	20	20	20	0	0	20	25	25	
organic textiles	7	7	7	7	7	7	7	7	
ferrite grains	40	40	20	40	60	40	0	0	
calcium silicate hydrate	CSH	xonotlite						CSH	
	10	10	5	30	10	0	0	10	
methyl cellulose	1	1	1	1	1	1	1	1	
mixing agent	0	0	25	0	0	10	37	27	
Water content of plate (water/solid)	62	64	56	76	61	51	60	71	Wt% in out side

[0030]

(Example 1)

The powder raw material was prepared as a combination of cement 22 weight parts, fly ash of 20 weight parts, organic textiles of 7 weight parts, ferrite grains of 40 weight parts, calcium silicate hydrate of 10 weight parts, and methyl cellulose of 1 weight part. The calcium silicate hydrate used here was quasicrystal CSH, which was obtained by blending silica stone powder and milk of lime so that CaO/SiO_2 was set to 0.83 by a mole ratio; preparing a stock slurry by addition of water; and, then, reacting it with water and heating for 3.0 hours at 180 °C, at 100 rpm. A preparation was prepared by adding water of 62 weight parts to the solid material of said powder raw material as 100, and mixed and kneaded for 10 minutes in a cement mixer at 50 rpm. Thereafter, a plate material of 450 mm of length, 300 mm of width, and 12 mm of thickness was obtained. Thereafter, the plate material was cured at 5 kgf/cm^2 for 10 hours with water and heating. An electromagnetic wave absorber was thus obtained.

[0031]

(Example 2)

The powder raw material was prepared as a combination of cement of

22 weight parts, fly ash of 20 weight parts, organic textiles of 7 weight parts, ferrite grains of 40 weight parts, calcium silicate hydrate of 10 weight parts, and methyl cellulose of 1 weight part. The calcium silicate hydrate used here was crystalline xonotlite which was obtained by blending silica stone powder and milk of lime so that CaO/SiO_2 was set to 1.00 by a mole ratio; preparing a starting slurry material by addition of water at 25 fold in weight; and, then, reacting it with water and heating for 8.0 hours at 205 °C, at 100 rpm in an stirring autoclave. A preparation was prepared by adding water of 64 weight parts to the solid material of said powder raw material as 100, and an electromagnetic wave absorber was thus obtained in the same manner as Example 1.

[0032]

(Example 3)

The powder raw material was prepared as a combination of cement of 22 weight parts, fly ash of 20 weight parts, organic textiles of 7 weight parts, ferrite grains of 20 weight parts, calcium silicate hydrate of 5 weight parts, methyl cellulose of 1 weight part and an mixing agent of 25 weight parts. The calcium silicate hydrate used here was crystalline xonotlite used in Example 1. A preparation was prepared by adding water of 64 weight parts to the solid material of said powder raw material as 100, and an electromagnetic wave absorber was thus obtained in the same manner as Example 1.

[0033]

(Example 4)

The powder raw material was prepared as a combination of cement of 22 weight parts, organic textiles of 7 weight parts, ferrite grains of 40 weight parts, calcium silicate hydrate of 30 weight parts, and methyl cellulose of 1 weight part. The calcium silicate hydrate used here was crystalline xonotlite used in Example 1. A preparation was prepared by adding water of 76 weight parts to the solid material of said powder raw material as 100, and an electromagnetic wave absorber was thus obtained in the same manner as Example 1.

[0034]

(Example 5)

The powder raw material was prepared as a combination of cement of 22 weight parts, organic textiles of 7 weight parts, ferrite grains of 60 weight parts, calcium silicate hydrate of 10 weight parts, and methyl cellulose of 1 weight part. The calcium silicate hydrate used here was crystalline xonotlite used in Example 1. A preparation was prepared by adding water of 61 weight parts to the solid material of said powder raw material as 100, and an electromagnetic wave absorber was thus obtained in the same manner as Example 1.

[0035]

The comparative examples against the above-mentioned examples are explained below.

(Comparative example 1)

The powder raw material was prepared as a combination of cement of 22 weight parts, fly ash of 20 weight parts, organic textiles of 7 weight parts, ferrite grains of 40 weight parts, methyl cellulose of 1 weight part and an mixing agent of 10 weight parts. A preparation was prepared by adding water of 51 weight parts to the solid material of said powder raw material as 100, and an electromagnetic wave absorber was thus obtained in the same manner as Example 1.

[0036]

(Comparative example 2)

The powder raw material was prepared as a combination of cement of 30 weight parts, fly ash of 25 weight parts, organic textiles of 7 weight parts, methyl cellulose of 1 weight part and an mixing agent of 37 weight parts. A preparation was prepared by adding water of 60 weight parts to the solid material of said powder raw material as 100, and an electromagnetic wave absorber was thus obtained in the same manner as Example 1.

[0037]

(Comparative example 3)

The powder raw material was prepared as a combination of cement of 30 weight parts, fly ash of 25 weight parts, organic textiles of 7 weight parts, calcium silicate hydrate of 10 weight parts, methyl cellulose of 1 weight part and

an mixing agent of 27 weight parts. The calcium silicate hydrate used here was quasicrystal CSH used in Example 1. A preparation was prepared by adding water of 71 weight parts to the solid material of said powder raw material as 100, and an electromagnetic wave absorber was thus obtained in the same manner as Example 1.

[0038]

(Measurement of physical properties)

As the electromagnetic wave absorbers obtained in the above-mentioned Examples 1-5 and the comparative examples 1-3, the bulk specific gravity, bending strength, water absorption, and a water absorption length rate of change were measured. The specific strength was calculated by (bending strength)/(specific gravity)^2. The measurement results are shown in Table 2.

[0039]

[Table 2]

	Examples					Comparative examples			Remark
	1	2	3	4	5	1	2	3	
bulk specific gravity	1.18	1.08	1.12	0.71	1.37	1.76	1.17	0.81	JISA5430
bending strength	117	86	106	40	129	146	132	94	JIS A1408
Specific strength	84	73	65	79	68	47	100	143	JIS A5430
water absorption	20	22	20	42	18	16	28	37	JIS A5430
length change rate at water	0.159	0.164	0.162	0.277	0.153	0.152	0.166	0.260	JIS A5430

absorption									

[0040]

Here, measurement of said bulk specific gravity was carried out based on JISA5430. Measurement of said bending strength was carried out based on JIS A1408. The unit is kgf/cm^2. Measurement of said water absorption was carried out based on JIS A5430. The unit is wt%. Said length change rate at water absorption was measured based on JIS A5430. The unit is %.

[0041]

(Electromagnetic-wave-absorbing performance of an electromagnetic wave absorber)

The measurement results of the electromagnetic-wave-absorbing performance of the electromagnetic wave absorber containing the ferrite in the above-mentioned examples and the comparative examples are shown in Fig. 1. Fig. 1 shows the reflection loss over the electromagnetic waves of the electromagnetic wave absorber containing 40 wt% of ferrite in Examples 1, 2, and 4 and the comparative example 1. The reflection loss (dB) of the electromagnetic waves which reflected from the electromagnetic wave absorber is set in the vertical axis, while the frequency (Hz) of the electromagnetic waves which entered into the electromagnetic wave absorber was set as a horizontal axis. When 40 wt% of the ferrite grains were contained, it is clear that the reflecting loss was remarkable at or near 4.5 GHz regarding the electromagnetic-wave-absorbing performance of an electromagnetic wave absorber as shown in Fig. 1. That is, the electromagnetic waves which entered into the electromagnetic wave absorber were remarkably absorbed by the electromagnetic wave absorber in an about 4.5-GHz frequency domain. Therefore, it was checked that electromagnetic-wave-absorbing performance is securable for an electromagnetic wave absorber by containing a ferrite.

[0042]

The following matters were confirmed by checking the measurement results of the physical properties of the electromagnetic wave absorber in each of the above-mentioned Examples 1-5 and the comparative examples 1-3.

1. Regarding the bulk specific gravity of the electromagnetic wave

absorbers containing 40 wt% of ferrite in Examples 1, 2, and 4 and the comparative example 1, as shown in Table 2, Comparative example 1 provided 1.76 g/cm^3, while Example 1 provided 1.18 g/cm^3, Example 2 provided 1.08 g/cm^3, and Example 4 provided 1.12 g/cm^3. Therefore, it was confirmed that the weight saving of the electromagnetic wave absorber in this invention had been attained.

[0043]

2. The bending strengths of the electromagnetic wave absorbers in Examples 1 and 3 was 117 kgf/cm^2 in Example 1, as shown in Table 2, and, in Example 3, it was 106 kgf/cm^2. Since such a property value satisfied that of a calcium silicate board (bulk specific gravity 0.6 - 1.2 g/cm^3, bending strength of 102 kgf/cm^2) as a fire-proof-protection board, it was confirmed that the electromagnetic wave absorbers in Examples 1 and 3 were effective as a fire-proof-protection board.

[0044]

3. Regarding the bending strengths of the electromagnetic wave absorbers in Examples 1 and 2, it was 117 kgf/cm^2 in Example 1 containing CSH of 10 wt%, while 86 kgf/cm^2 in Example 2 containing xonotlite of 10 wt%. Therefore, it was confirmed by the calcium silicate hydrate adopted as a powder raw material that CSH is desirable.

[0045]

4. In the electromagnetic wave absorber of the comparative example 1, since it contained the ferrite, and an electromagnetic wave absorber had an increase in specific gravity and the thermal conductivity of the electromagnetic wave absorber increased. Insulation efficiency reduced as an electromagnetic wave absorber. On the other hand, in the electromagnetic wave absorber in Examples 1 and 2, since the ultralight calcium silicate hydrate was used, the electromagnetic wave absorbers had no increase in their specific gravities, and did not increase the thermal conductivities. Therefore, it was confirmed that the insulation efficiency of the electromagnetic wave absorbers were not reduced.

[0046]

The crystal water of the calcium silicate hydrate can be changed with

kinds of calcium silicate hydrate like CSH, xonotlite (6CaO, $6SiO_2$, and H_2O), and tobermorite (5CaO, $6SiO_2$, and $5H_2O$). Therefore, the heat resistance of an electromagnetic wave absorber can be operated by changing the kind of calcium silicate hydrate, i.e., change the quantity of crystal water to hold.

[0047]

[Effect of the Invention]

The electromagnetic wave absorber of this invention contains 20 to 60 wt% of the ferrite, as well as calcium silicate hydrate of a bulk specific gravity of 0.15 or less in an amount of 5 to 30 wt%. For this reason, by the ultralight calcium silicate hydrate, the weight increasing of the electromagnetic wave absorber by the ferrite content can be controlled, and a weight saving can be attained. Since it can fabricate using extrusion molding, drying shaping, etc. and also a certain water heat treatment can also be performed from the former, the manufacturing efficiency of an electromagnetic wave absorber can be raised.

[Fig. 1]